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(54) Title: POLYMERIZATION OF VINYL ETHERS

(57) Abstract

Provided is a method for the polymerization of vinyl ethers catalyzed by complexes of a lithium salt and a polyether. A preferred complex is a complex of lithium tetrafluoroborate and a glyme. The resulting polymers are produced under mild and controlled conditions and are useful in adhesives and coatings as well as in other uses such as for polymer electrolytes in batteries and for viscosity modifiers.

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POLYMERIZATION OF VINYL ETHERS

RELATED APPLICATION

This application claims priority to U.S. application serial number 09/093,527 filed 08 June 1998.

TECHNICAL FIELD

The present invention relates generally to the field of polymers and to methods for polymerizing monomers for the production of polymers. More particularly, this invention pertains to methods for the polymerization of vinyl ethers catalyzed by complexes of lithium salts and polyethers.

BACKGROUND

Throughout this application, various publications, patents, and published patent applications are referred to by an identifying citation. The disclosures of the publications, patents, and published patent applications referenced in this application are hereby incorporated by reference into the present disclosure to more fully describe the state of the art to which this invention pertains.

Vinyl ether polymers have found many uses in various applications such as, for example, coatings, tackifiers in adhesives, additives to lubricating oils and brake fluids, corrosion inhibitors, viscosity modifiers, and medical uses, as for example described in *Encyclopedia of Physical Science and Technology, Vol. 1,* page 63 (1992), Academic Press, Inc., by Tedeshi. A more recent application for vinyl ether polymers has been as polymer electrolytes in lithium batteries, as for example described in U.S. Pat. No. 5,411,819 to Marchese *et al.* In addition, vinyl ether polymers have found applications in modifying the properties of other polymers, such as, for example, polyvinyl chloride, polyacrylonitrile, and polyethylene, when incorporated by physical mixture or block copolymerization, even in relatively small amounts. These benefits by blending or by

block copolymerization of vinyl ether polymers include improved processability, reduced costs of production, plasticizing properties, stabilizing properties, and improved heat resistance, adhesive, and other properties.

Vinyl ether polymers for various applications are commonly prepared by a process of cationic polymerization under the catalytic effect of Brønsted (protonic) acids, such as, for example, trifluoromethanesulfonic acid and HI/I_2, or of Lewis (non-protonic) acids, such as, for example, halides of zinc, iron, tin, boron, and aluminum. A series of BF_3 compounds, such as, for example, complexes with aliphatic and cyclic ethers, are widely accepted among the Lewis acid-type polymerization catalysts for polymerization of vinyl ethers. Their acidic character is a common feature of the catalysts for cationic polymerization of vinyl ethers, as, for example, described in U.S. Pat. No. 5,147,963 to Plochocka *et al.* Also, for example, U.S. Pat. No. 5,055,536 to Dubois describes a process for the polymerization of vinyl ethers catalyzed by an acidic zeolite and an iodine containing electrophile.

Inorganic salts, where the anion of the salt is the anion of an acid capable of catalyzing the polymerization of vinyl ethers, have been reported for use in the polymerization of vinyl ethers. For example, U.S. Pat. No. 5,475,069 to Drysdale describes the liquid phase polymerization of selected vinyl ethers catalyzed by yttrium or other rare earth metal perfluoroalkylsulfonates, which may also optionally contain neutral ligands, for example, water and ethers, such as dimethyl ether, which are usually coordinated with the metal cation. Also, for example, U.S. Pat. No. 5,411,819 to Marchese *et al.* discloses that a mixture of a vinyl ether and a divinyl ether, when combined with lithium tetrafluoroborate in the amount of 1 to 30 % by weight and applied onto an inert support, polymerizes spontaneously at room temperature to prepare a solid, polyvinyl ether-based polymeric electrolyte in a membrane form. An oligomer, such as polyethylene glycol or tetraglyme, or a dipolar aprotic liquid, such as propylene carbonate, may optionally be present, but is not required.

The cationic polymerization of vinyl ethers is typically carried out in a liquid solution at various temperatures ranging from -80 °C to the boiling point of the vinyl ether monomer. The molecular weight and properties of the vinyl ether polymer depend on the

type of polymerization catalyst and the reaction temperature. Cationic polymerization to prepare vinyl ether polymers, particularly in the large scale desired for commercial production, generates a considerable amount of heat due to the high heats of exothermic reaction for the polymerization of vinyl ether monomers. Thus, the production of vinyl ether polymers by cationic polymerization encounters quality issues related to monitoring and controlling the exothermic polymerization process, non-uniform distribution of the catalyst, localized areas of polymerization with local areas of overheating as a result, and side reactions. For example, U.S. Pat. No. 5,616,812 to Egawa *et al.* describes a method for controlling the polymerization of vinyl ethers by utilizing the presence of a Lewis acid catalyst and a specific acetal with a vinyl ether compound.

Since the properties of vinyl ether polymers depend significantly on the catalyst utilized in their production, it would be advantageous if a polymerization catalyst were available that is latent or at least relatively inactive at room temperature, but is activated at a higher temperature, such as for example 50 °C to 70 °C, to provide a well-controlled polymerization process over a wide temperature range above the activation temperature. Polymerization catalysts of this type would find use in the production of vinyl ether polymers and copolymers with higher quality, higher yields, and potentially new properties to extend the fields of their application, such as, for example, in the development of thermally-activated single-component adhesive and sealing agents, and in the development of vinyl ether polymer electrolytes for batteries, including thermally activated processes for producing the polymers in the electrolytes.

SUMMARY OF THE INVENTION

One aspect of the present invention pertains to a method for the polymerization of vinyl ethers to form a poly(vinyl ether) comprising contacting one or more vinyl ethers with a complex of a lithium salt and a polyether to form a mixture, wherein the one or more vinyl ethers are present in a liquid phase; and heating the mixture to a temperature sufficient to polymerize the one or more vinyl ethers and form the poly(vinyl ether).

In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 2.5 per cent by weight of the one or more vinyl ethers. In one

embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 2.3 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 2.0 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 1.6 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 1.2 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 0.9 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex is present in an amount of 0.01 to 0.6 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex is present in an amount of 0.01 to 0.3 per cent by weight of the one or more vinyl ethers.

This method provides an effective polymerization by allowing the synthesis to be carried out under mild, uniform, and controlled reaction conditions which result in high production yields of the desired vinyl ether polymer product.

A large number of lithium salts, which have anions which are also the anions of acids capable of catalyzing the polymerization of vinyl ethers, are suitable for use in the present invention. In one embodiment, the lithium salt is lithium imide. In one embodiment, the lithium salt is a lithium perfluoroalkylsulfonate, preferably lithium triflate. In a preferred embodiment, the lithium salt is lithium tetrafluoroborate.

In one embodiment, the polyether is an aliphatic polyether having two or more ether functional groups, wherein at least two of said two or more ether functional groups are characterized by an oxygen atom covalently bonded via single bonds to a first carbon atom and a second carbon atom, and wherein each of the first and second carbon atoms are further covalently bonded via single bonds to three atoms selected from the group consisting of: carbon, hydrogen, oxygen, chlorine, fluorine, and bromine. In a preferred embodiment, this aliphatic polyether is a glyme, and more preferably, this aliphatic polyether is selected from the group consisting of: monoglyme, diglyme, triglyme, and tetraglyme.

In one embodiment, the molar ratio of the polyether to the lithium salt in the complex is 2 to 1. In one embodiment, the molar ratio of the polyether to the lithium salt in the complex of this invention is 1.33 to 1. In one embodiment, the molar ratio of the polyether to the lithium salt in the complex of this invention is 1 to 1. In one embodiment, the molar ratio of the polyether to the lithium salt in the complex of the present invention is less than 1 to 1.

In one embodiment, the one or more vinyl ethers comprise one or more monovinyl ethers. In one embodiment, the one or more vinyl ethers is a monovinyl ether selected from the group consisting of: (a) methyl vinyl ether, (b) ethyl vinyl ether (EVE), (c) propyl vinyl ether (PVE), (d) butyl vinyl ether (BVE), (e) isobutyl vinyl ether, (f) 2-ethylhexyl vinyl ether, (g) cyclohexyl vinyl ether (CHE), (h) 2,2,3,3-tetrafluoropropanol vinyl ether (FVE), (i) ethylene glycol vinyl glycidyl ether (VGE), (j) propylene glycol vinyl glycidyl ether (PGVGE), (k) 3-(2-vinyloxyethoxy)propylene-1,2-carbonate (VPC), (l) triethylene glycol vinyl ether (TVE), (m) 1,4-butanediol vinyl ether (BDVE), (n) vinyl ether of diethylene glycol diacetal (VDA), (o) vinyl ether of diethylene glycol triacetal, (p) vinyl allyl diether of ethylene glycol (VADE), and (q) vinyl propargyl diether of ethylene glycol (VPDE).

In another embodiment of the method of this invention, the one or more vinyl ethers comprise one or more divinyl ethers. In one embodiment, the one or more vinyl ethers is a divinyl ether selected from the group consisting of: (a) ethylene glycol divinyl ether (EDVE), (b) 1,4-butanediol divinyl ether (BDDVE), (c) diethylene glycol divinyl ether (DDVE), (d) triethylene glycol divinyl ether (TDVE), (e) tetraethylene glycol divinyl ether, (f) 1,4-cyclohexanedimethanol divinyl ether, (g) diethylene glycol diacetal divinyl ether (DEDA), and (h) diethylene glycol triacetal divinyl ether.

In another embodiment of the method of this invention, the one or more vinyl ethers comprise one or more polyvinyl ethers. In one embodiment, the one or more vinyl ethers is pentaerythritol tetravinyl ether (PTVE).

In one embodiment, the mixture of one or more vinyl ethers with a complex of a lithium salt and a polyether further comprises a solvent. In a preferred embodiment, the

solvent comprises a polyether, and more preferably, the polyether of the solvent is the same as the polyether of the complex of a lithium salt and a polyether of this invention. In a most preferred embodiment, the complex of the method of this invention is present in the amount of 1 to 35 per cent by weight of the polyether of the solvent.

In one embodiment, the heating step is carried out at a temperature of polymerization from 20 °C to 120 °C and, preferably, at a temperature of polymerization from 35 °C to 120 °C. In a more preferred embodiment, the heating step is carried out at a temperature of polymerization from 50 °C to 120 °C, and, most preferably, the heating step is carried out at a temperature of polymerization from 70 °C to 120 °C. The methods of the present invention typically still function at a temperature of polymerization of greater than 120 °C, and such a temperature may be desirable if, for example, shorter time periods for the polymerization are required.

In a preferred embodiment, a mixture of one or more vinyl ethers and a complex of a lithium salt and a polyether is formed at a first temperature of about 25 °C or lower, wherein the one or more vinyl ethers are present in a liquid phase, and wherein the mixture does not significantly polymerize if kept at a temperature of 25 °C over a period of 36 hours; and subsequently, the mixture is heated to a second temperature greater than 35 °C to polymerize the one or more vinyl ethers and form the poly(vinyl ether). Preferably, the heating to polymerize the one or more vinyl ethers is carried out at a second temperature from 35 °C to 120 °C. More preferably, the heating to polymerize the one or more vinyl ethers is carried out at a second temperature greater than 50 °C, such as from 50 °C to 120 °C. Most preferably, the heating to polymerize the one or more vinyl ethers is carried out at a second temperature greater than 70 °C, such as from 70 °C to 120 °C or at even higher temperatures if, for example, a faster rate of polymerization is desired. This aspect of the method provides a heat-activated polymerization where the complex of a lithium salt and a polyether is latent or inactive as a polymerization catalyst at 25 °C, but is effective in catalyzing the polymerization of the one or more vinyl ethers at a temperature greater than 35 °C.

Additional preferred embodiments are described below. As will be appreciated by one of skill in the art, features of one aspect or embodiment of the invention are also applicable to other aspects or embodiments of the invention.

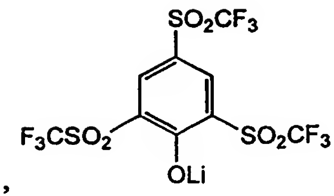
DETAILED DESCRIPTION OF THE INVENTION

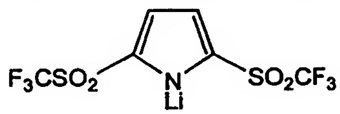
One aspect of the present invention pertains to a method for the polymerization of vinyl ethers to form a poly(vinyl ether), comprising contacting one or more vinyl ethers with a complex of a lithium salt and a polyether to form a mixture, wherein the one or more vinyl ethers are present in a liquid phase, and wherein the complex is present in an amount of 0.01 to 2.5 per cent by weight of the one or more vinyl ethers; and heating the mixture to a temperature sufficient to polymerize the one or more vinyl ethers and form the poly(vinyl ether).

Polyether Lithium Salt Complexes

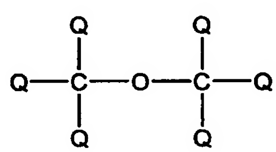
The phrases "polyether lithium salt complex" and "complex of a lithium salt and a polyether," as used herein, relate to a chemical species which may conveniently be referred to as a complex or a coordination compound and which comprises the chemical constituents of one or more lithium salts (*e.g.*, LiA or Li^+A^-, comprising a lithium cation, Li^+, and an anion, A^-) and one or more polyethers. It may be convenient to consider the complex as comprising one or more complex cations and one or more salt anions, A^-, wherein the complex cations comprise one or more lithium ions, Li^+, and one or more polyether ligands coordinated to the lithium ion or ions. In most cases, the polyether ligands are coordinated to one or more lithium ions via one or more of the oxygen atoms of the polyether.

Suitable lithium salts for use in the complexes of the method of the present invention include, but are not limited to, $LiBF_4$, $LiSO_3CF_3$, $LiSO_3CF_2CF_3$, $LiSO_3CF_2CF_2CF_3$, $LiN(SO_2CF_3)_2$, $LiPF_6$, $LiAlCl_4$, $LiAsF_6$, $LiSbF_6$, $LiSbCl_6$, $LiClO_4$,

$LiSO_3CH_3$, $LiC(SO_2CF_3)_3$, $LiNSO_2CF_2CF_2CF_2CF_2SO_2$,  ,

 , and combinations thereof. Preferred lithium salts for use in this invention are $LiBF_4$ (lithium tetrafluoroborate); lithium perfluoroalkylsulfonates with one to thirty carbon atoms in the alkyl group, such as, for example, $LiSO_3CF_3$ (lithium triflate); and $LiN(SO_2CF_3)_2$ (lithium imide). Most preferably, the lithium salt is $LiBF_4$.

The terms "polyether" and "polyethers," as used herein, both pertain to molecules having two or more ether functional groups, wherein at least two of the two or more ether groups are of the formula shown below, that is, are characterized by an oxygen atom, O, with single bonds to two carbon atoms, C, which carbon atoms have only single bonds to atoms, denoted Q, selected from the group consisting of: carbon, C; hydrogen, H; oxygen, O; and halogen, such as chlorine, Cl, fluorine, F, and bromine, Br.



Suitable polyethers for use in the complexes of the method of this invention include, but are not limited to:

(a) the dimethyl ethers of an aliphatic diol, for example, the dimethyl ethers of ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, and 1,8-octanediol;

(b) the dimethyl ethers of polyalkylene glycols, for example, the dimethyl ethers of diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, nonaethylene glycol, decaethylene glycol, and further polyalkylene glycols up to a molecular weight of about 6000;

(c) the diethyl ethers of an aliphatic diol, for example, the diethyl ethers of ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, and 1,8-octanediol;

(d) the diethyl ethers of polyalkylene glycols, for example, the diethyl ethers of diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, nonaethylene glycol, decaethylene glycol, and further polyalkylene glycols up to a molecular weight of about 6000;

(e) the divinyl ethers of polyalkylene glycols, for example, the divinyl ethers of diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, nonaethylene glycol, decaethylene glycol, and further polyalkylene glycols up to a molecular weight of about 6000;

(f) the divinyl ethers of polyalkylene glycols polyacetals, for example, the divinyl ethers of diethylene glycol diacetal and diethylene glycol triacetal, and further polyalkylene glycols polyacetals up to a molecular weight of about 6000; and,

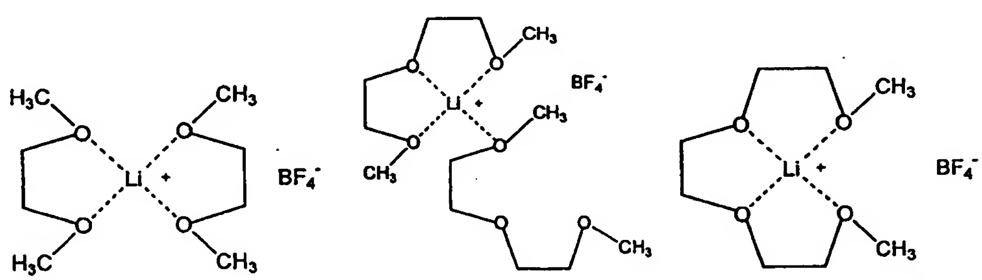
(g) cyclic polyethers such as, for example, 1,3-dioxane, 1,4-dioxane, and 1,3-dioxolane.

Preferred polyethers for use in this invention are the dimethyl ethers of ethylene glycol and of polyalkylene glycols, which are collectively referred to herein as a class by the terms "glyme" and "glymes." For example, the dimethyl ether of ethylene glycol is monoglyme (*i.e.*, CH_3-O-CH_2CH_2-O-CH_3); the dimethyl ether of diethylene glycol is diglyme (*i.e.*, CH_3-O-$(CH_2CH_2$-$O)_2$-CH_3); the dimethyl ether of triethylene glycol is triglyme (*i.e.*, CH_3-O-$(CH_2CH_2$-$O)_3$-CH_3); and the dimethyl ether of tetraethylene glycol is tetraglyme (*i.e.*, CH_3-O-$(CH_2CH_2$-$O)_4$-CH_3). More preferably, the polyethers employed in the invention are selected from the group consisting of: monoglyme, diglyme, triglyme, and tetraglyme.

In a complex of a lithium salt and a polyether, the molar ratio of polyether to lithium salt is usually 2:1 or less, and may be fractional. For example, a complex may be formed from a lithium salt, LiA, and a polyether having only two ether groups (and thus only two ether oxygen atoms) in which two polyether molecules are coordinated around a

single lithium cation, as in, for example, $Li(L)_2^+ A^-$, wherein L denotes the polyether ligand and A denotes the lithium salt anion. In this case, the molar ratio of polyether to lithium salt is 2:1. Similarly, a complex may be formed from a lithium salt, LiA, and a polyether having four ether groups (and thus four ether oxygen atoms) in which one polyether molecule is coordinated around a single lithium cation, as in, for example, $Li(L)^+ A^-$, wherein L denotes the polyether ligand and A denotes the lithium salt anion. In this case, the molar ratio of polyether to lithium salt is 1:1. For polyethers having more than four ether functional groups, the resulting complex may comprise more than one lithium cation, and accordingly the molar ratio of the polyether to the lithium salt may become less than 1:1, and progressively further less than 1:1 as the number of ether functional groups per molecule increases. For example, a complex may be formed from a lithium salt, LiA, and a polyether having eight ether groups (and thus eight ether oxygen atoms) in which one polyether molecule is coordinated to two lithium cations, as in, for example, $Li_2(L)^{+2}(A^-)_2$, wherein L denotes the polyether ligand and A denotes the lithium salt anion. In this case, the molar ratio of polyether to lithium salt is 0.5:1.

Examples of complexes of a lithium salt and a polyether include complexes of the lithium salt $LiBF_4$ with the polyethers monoglyme, diglyme, and triglyme. A complex formed from $LiBF_4$ and two molecules of monoglyme is shown below as formula **I**. A complex formed from $LiBF_4$ and two molecules of diglyme is shown below as formula **II**. A complex formed from $LiBF_4$ and one molecule of triglyme is shown below as formula **III**.

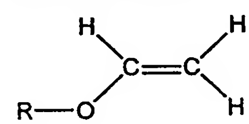


I II III

Vinyl Ether Polymerization

The polyether lithium salt complexes described herein are particularly useful as catalysts or initiators for the polymerization of vinyl ethers. The polyether lithium salt complexes are typically stable in air and are non-volatile, and the polymerization process is consequently more convenient and easier to control, especially in regard to the delivery of catalysts, control of the amount of the catalyst, and the distribution of the catalyst. These and other properties offer substantial advantages compared to the conventional catalysts, such as ether complexes of boron trifluoride and related Lewis acid complexes, which typically exhibit instability in air and fuming. Furthermore, the use of polyether lithium salt complexes, which are typically soluble in the vinyl ether monomer, significantly reduces the possibility of localized polymerization and related inhomogeneity of polymer properties, resinification, overheating, and other process variations.

The term "vinyl ether," as used herein, relates to a chemical compound which comprises at least one unsubstituted vinyl group (*i.e.*, $-CH=CH_2$) covalently bonded to the oxygen of an ether group. Thus, generic vinyl ethers may be represented by the general formula $R-O-CH=CH_2$, which is also illustrated below.



In this formula, R denotes a chemical moiety which, together with the vinyl group and the oxygen atom, forms a molecule with an ether group (*i.e.*, C-O-C), that is, the ether oxygen atom is covalently bonded to a carbon atom of the R group.

When only one vinyl ether group is present in the vinyl ether molecule, it is referred to herein by the term "monovinyl ether." When two vinyl ether groups are present in the vinyl ether molecule, it is referred to herein by the term "divinyl ether."

In the above formula, R may vary widely. Examples of suitable R groups include, but are not limited to, aliphatic, alicyclic, and aromatic groups comprising at least one carbon atom, which may be substituted or unsubstituted. Examples of aliphatic groups

include, but are not limited to, linear or branched alkyl groups having from 1 to 30 carbon atoms, more preferably from 1 to 12 carbon atoms, and most preferably from 1 to 6 carbon atoms, such as methyl, ethyl, propyl, and butyl. Examples of alicyclic groups include, but are not limited to, cyclic alkyl groups having from 3 to 15, more preferably from 3 to 8 carbons atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Examples of aromatic groups include, but are not limited to, phenyl and benzyl. Examples of suitable substituents are those that are inert or relatively inert during the polymerization process, and include, but are not limited to, ether, halo, keto, ester, amide, silyl, carbonate, olefinic, aromatic, and acetylenic groups.

Examples of suitable vinyl ethers include, but are not limited to, monovinyl ethers such as:

(a) methyl vinyl ether,

$$CH_3{-}O{-}CH{=}CH_2$$

(b) ethyl vinyl ether (EVE),

$$CH_3CH_2{-}O{-}CH{=}CH_2$$

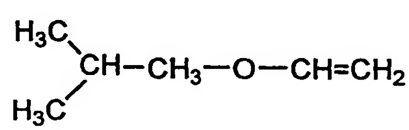
(c) propyl vinyl ether (PVE),

$$CH_3CH_2CH_2{-}O{-}CH{=}CH_2$$

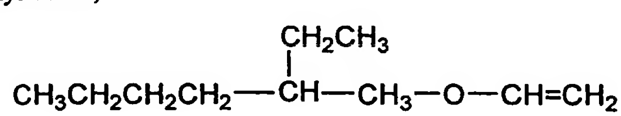
(d) butyl vinyl ether (BVE),

$$CH_3CH_2CH_2CH_2{-}O{-}CH{=}CH_2$$

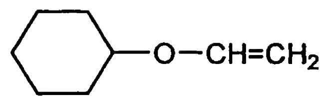
(e) isobutyl vinyl ether,



(f) 2-ethylhexyl vinyl ether,



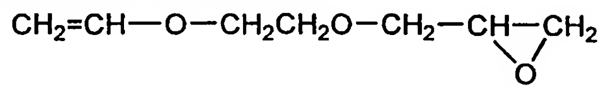
(g) cyclohexyl vinyl ether (CHE),



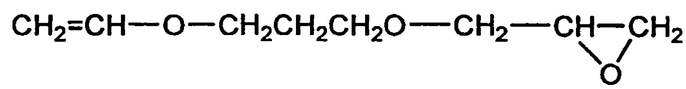
(h) 2,2,3,3-tetrafluoropropanol vinyl ether (FVE),

$$CF_2H-CF_2-CH_2-O-CH=CH_2$$

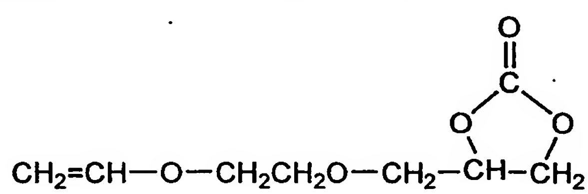
(i) ethylene glycol vinyl glycidyl ether (VGE),



(j) propylene glycol vinyl glycidyl ether (PGVGE),



(k) 3-(2-vinyloxyethoxy)propylene-1,2-carbonate (VPC),



(l) triethylene glycol vinyl ether (TVE),

$$HO-CH_2CH_2O-CH_2CH_2O-CH_2CH_2O-CH=CH_2$$

(m) 1,4-butanediol vinyl ether (BDVE),

$$HO-CH_2CH_2CH_2CH_2-O-CH=CH_2$$

(n) vinyl ether of diethylene glycol diacetal (VDA),

$$CH_2=CH-O\left(CH_2CH_2-O-CH_2CH_2-O-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-O\right)_2CH_2CH_2-O-CH_2CH_2-OH$$

(o) vinyl ether of diethylene glycol triacetal,

$$CH_2{=}CH{-}O{-}\left(CH_2CH_2{-}O{-}CH_2CH_2{-}O{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}O\right)_3{-}CH_2CH_2{-}O{-}CH_2CH_2{-}OH$$

(p) vinyl allyl diether of ethylene glycol (VADE),

$$CH_2{=}CH{-}CH_2{-}O{-}CH_2CH_2O{-}CH{=}CH_2$$

(q) vinyl propargyl diether of ethylene glycol (VPDE),

$$CH{\equiv}C{-}CH_2{-}O{-}CH_2CH_2O{-}CH{=}CH_2$$

Additional examples of suitable vinyl ethers include, but are not limited to, divinyl ethers such as:

(a) ethylene glycol divinyl ether (EDVE),

$$CH_2{=}CH{-}O{-}CH_2CH_2O{-}CH{=}CH_2$$

(b) 1,4-butanediol divinyl ether (BDDVE),

$$CH_2{=}CH{-}O{-}CH_2CH_2CH_2CH_2{-}O{-}CH{=}CH_2$$

(c) diethylene glycol divinyl ether (DDVE),

$$CH_2{=}CH{-}O{-}CH_2CH_2O{-}CH_2CH_2O{-}CH{=}CH_2$$

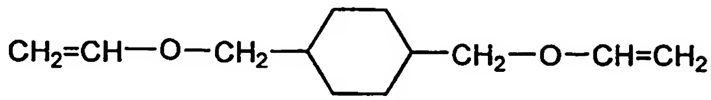
(d) triethylene glycol divinyl ether (TDVE),

$$CH_2{=}CH{-}O{-}CH_2CH_2O{-}CH_2CH_2O{-}CH_2CH_2O{-}CH{=}CH_2$$

(e) tetraethylene glycol divinyl ether,

$$CH_2{=}CH{-}O{-}CH_2CH_2O{-}CH_2CH_2O{-}CH_2CH_2O{-}CH_2CH_2O{-}CH{=}CH_2$$

(f) 1,4-cyclohexanedimethanol divinyl ether,



(g) diethylene glycol diacetal divinyl ether (DEDA),

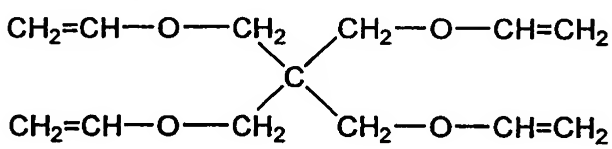
$$CH_2{=}CH{-}O{-}\left(CH_2CH_2{-}O{-}CH_2CH_2{-}O{-}\underset{}{\overset{CH_3}{\overset{|}{C}}}H{-}O\right)_2{-}CH_2CH_2{-}O{-}CH_2CH_2{-}O{-}CH{=}CH_2$$

(h) diethylene glycol triacetal divinyl ether,

$$CH_2{=}CH{-}O{-}\left(CH_2CH_2{-}O{-}CH_2CH_2{-}O{-}\underset{}{\overset{CH_3}{\overset{|}{C}}}H{-}O\right)_3{-}CH_2CH_2{-}O{-}CH_2CH_2{-}O{-}CH{=}CH_2$$

Additional examples of suitable vinyl ethers include, but are not limited to, polyvinyl ethers such as:

(a) pentaerythritol tetravinyl ether (PTVE),



The versatility of the catalytic and/or initiating effect of polyether lithium salt complexes for the effective polymerization of many of the foregoing vinyl ethers has been demonstrated herein.

In those cases where the vinyl ether is also a polyether, as defined herein, it may serve both as a vinyl ether monomer for polymerization and also as polyether ligand in a polyether lithium salt complex.

When one or more different vinyl ethers, such as one or more monovinyl ethers or one or more divinyl ethers, or a vinyl ether with a non-vinyl ether containing reactive group or moiety, are utilized in the method of the present invention, copolymers are

formed which may be of block or random bonding sequences and may be of linear, branched, or radial structures.

Vinyl Ether Polymerization: Reaction Conditions

In the vinyl ether polymerization methods of the present invention, the one or more vinyl ethers are present in a liquid phase. The one or more vinyl ethers may themselves be a liquid at the temperature and pressure of the polymerization reaction, and thus be present in a liquid phase. Alternatively, the vinyl ether may present in a solution which is a liquid at the temperature and pressure of the polymerization reaction, and thus be present in a liquid phase.

Although not essential, it is preferred that the polyether lithium salt complex is also present in the liquid phase. In any case, the polyether lithium salt complex must be in contact with the vinyl ether. For example, at room temperature and atmospheric pressure, the lithium salt $LiBF_4$ is poorly soluble in many vinyl ethers and remains as insoluble crystals. As such, the $LiBF_4$ is not effective in initiating controlled polymerization of vinyl ethers. However, many polyether $LiBF_4$ complexes, such as an ethylene glycol dimethyl ether $LiBF_4$ complex (see Formula I shown above), are soluble in many vinyl ethers and thus are effective as catalysts for the polymerization of vinyl ethers. Such complexes permit the polymerization process to be carried out under mild conditions (*e.g.*, a temperature in a range of about 35 °C to 70 °C, though the reaction temperature may be higher or lower), with concentrations of the complex (catalyst) of as low as only 0.01 to 2.5 per cent by weight of the vinyl ether(s), and to be completed in a typically short reaction time (*e.g.*, about 0.1 to 3 hours, though the reaction time may be shorter or longer).

Suitable concentrations of the polyether lithium salt complex for the polymerization of the method of the present invention include, but are not limited to, the range of 0.01 to 2.5 per cent by weight of the vinyl ether. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 2.3 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 2.0 per cent by weight of the one or

more vinyl ethers. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 1.6 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 1.2 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex of a lithium salt and a polyether is present in an amount of 0.01 to 0.9 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex is present in an amount of 0.01 to 0.6 per cent by weight of the one or more vinyl ethers. In one embodiment, the complex of this invention is present in an amount of 0.01 to 0.3 per cent by weight of the one or more vinyl ethers.

For example, 0.5 per cent by weight of $LiBF_4$ (molecular weight of 93.74) complexed with 0.95 per cent by weight of diglyme (*i.e.*, the dimethyl ether of the polyalkylene glycol with the lowest molecular weigh, diethylene glycol) (molecular weight of 134.18), as shown in Formula II with a molar ratio of polyether to lithium salt of 1.33:1, in a mixture with the only other component being the one or more vinyl ethers to be polymerized, would have a weight per cent in the total mixture of 1.45 weight per cent (= 0.5 + 0.95) polyether lithium salt complex and 98.55 weight per cent of the one or more vinyl ethers. This equates to 1.47 weight per cent (= 1.45 / 98.55) of polyether lithium salt complex based on the weight of the one or more vinyl ethers.

Similarly, 1.0 per cent by weight of $LiBF_4$ complexed with 1.9 per cent by weight of triglyme (*i.e.*, the dimethyl ether of triethylene glycol) (molecular weight of 178.23), as shown in Formula III with a molar ratio of polyether to lithium salt of 1:1, in a mixture with the only other component being the one or more vinyl ethers to be polymerized, would have a weight per cent in the total mixture of 2.9 weight per cent (= 1.0 + 1.9) polyether lithium salt complex and 97.1 weight per cent vinyl ethers. This equates to 2.99 weight per cent (= 2.9 / 97.1) of polyether lithium salt complex based on the weight of the one or more vinyl ethers.

Suitable reaction temperatures for carrying out the polymerization of the present invention include, but are not limited to, the range of 20 °C to 120 °C. Preferably, the method of this invention is carried out at a temperature of from 35 °C to 120 °C; more preferably, from 50 °C to 120 °C and, most preferably, the method is carried out at a

temperature of from 70 °C to 120 °C. Preferably, the polymerization in the method of this invention does not occur significantly at room temperature such as, for example, over a 36 hour period at 25 °C, but occurs rapidly in a thermally-activated process at a higher temperature such as, for example, a temperature in the range of 35 °C to 120 °C. When the polyether lithium salt complex has this type of latent catalytic properties at 25 °C, the method of the present invention may be utilized to produce, by thermal activation at elevated temperatures, such as 35 °C and greater, a vinyl ether polymer product suitable for use in a range of applications where stronger adhesion, greatly increased viscosity, and other polyvinyl ether polymer properties, not present in the corresponding vinyl ether monomers, are desired in a thermally-activatible system.

Although this desired type of latent catalytic properties at 25 °C may exist with polyether lithium salt complexes at concentrations of 2 per cent by weight and higher based on the weight of the one or more vinyl ethers, lower concentrations of the polyether lithium salt complex, such as, for example, only 0.01 to 0.9 per cent by weight of the vinyl ether, enhance the likelihood of latent catalytic properties in that, at room temperature, the vinyl ether does not significantly polymerize, but, upon heating to a higher temperature, for example above 35 °C, preferably above 50 °C, and most preferably, above 70 °C, a rapid polymerization of the one or more vinyl ethers occurs. Low concentrations of catalyst are also advantageous in reducing the tendency of catalyst residues to contribute to oxidative and other instability of the polymer product and to corrosion of metals in contact with the polymer product.

Solutions of the polyether lithium salt complex may be prepared by dissolving the lithium salt in the polyether, such as, for example, dissolving $LiBF_4$ in the dimethyl ether of diethylene glycol.

The polymerization may be carried out with only the complex and the vinyl ether present, or preferably, with a solvent also present. Examples of suitable solvents include, but are not limited to, ethers with one ether functional group per molecule, such as ethyl ether; polyethers with two or more ether functional groups per molecule, such as monoglyme; aromatic hydrocarbons, such as toluene; chlorinated hydrocarbons, such as chloroform; and combinations thereof. Preferred solvents comprise polyethers, and most

preferably, the polyether used in the solvent is the same as the polyether in the complex with the lithium salt. When a polyether is present in the solvent of the present invention, suitable concentrations of the polyether lithium salt complex include, but are not limited to, 1 to 35 per cent by weight of the polyether that is present in the solvent, more preferably 1 to 10 per cent by weight of the polyether that is present in the solvent. At the lower concentrations, the latency of the catalyst at 25 °C is greater and the ability to more effectively introduce and control the amount of catalyst in the reaction mixture is enhanced.

The polymerization may be carried out under air or, preferably, under an inert or substantially inert gas, such as nitrogen or argon. The pressure during the polymerization process is not critical and may be atmospheric pressure, more than atmospheric pressure, or less than atmospheric pressure, but is preferably atmospheric pressure. The pressure in the reaction vessel may be that which is produced by the vapor pressure from the one or more vinyl ethers and any other volatile materials present.

It is preferred that the one or more vinyl ethers, the polyether lithium salt, and any other materials present in the reaction mixture be free or substantially free of water.

The polymerization process may be terminated by the addition of an alkali or basic material or by the addition of a protic material, such as methanol or water, optionally containing a small amount of a basic material, such as ammonia. Also, the vinyl ether polymer formed may be insoluble in the liquid phase of the reaction and may precipitate in a solid form, thereby effectively terminating its further polymerization. The starting materials are preferably added to the reaction vessel with agitation, and preferably, agitation may be continued during the polymerization process and during any process to terminate and reprecipitate the polymer for purification.

EXAMPLES

Several embodiments of the present invention are described in the following examples, which are offered by way of illustration and not by way of limitation.

Example 1

To 2.00 g of butyl vinyl ether (BVE), 0.0057 g of the complex of $LiBF_4$ with monoglyme (ethylene glycol dimethyl ether), as shown in Formula I, was added at 25 °C with stirring. This equates to 0.29 weight percent (wt%) of polyether lithium salt complex based on the weight of the vinyl ether. The mixture was then thermostatted at 50 °C for 40 minutes. The polymer of butyl vinyl ether thus prepared was dissolved in 6 ml of benzene and added with stirring into 70 ml of methanol containing 3 to 5 drops of aqueous ammonia. The polymer was then dried under vacuum (2 mm Hg) until a constant weight was obtained. Analysis of the polymer showed a colorless and transparent material with excellent solubility in benzene, acetone, dioxane, and chloroform, and with insolubility in methanol. The weight average molecular weight of the polymer was 101,000. The reprecipitated polymer contained no vinyl ether monomer, as confirmed by the lack of any C=C adsorption bands at 1620 to 1640 cm^{-1} in its infrared spectrum. The yield of the polymer was 1.86 g (93%). This example is summarized in Table 1.

Examples 2 - 23

An analogous procedure to that described in Example 1, except for the temperature of polymerization as noted below, was utilized for the polymerization of the vinyl ethers in Examples 2 - 23, as summarized in Table 1.

Example 24

An analogous procedure to that described in Example 1, except for the temperature of polymerization as noted in Table 2 below, was utilized for the polymerization of butyl vinyl ether (BVE) in the presence of 0.87 wt% (based on the weight of vinyl ether) of the complex of $LiBF_4$ with diglyme (diethylene glycol dimethyl ether), as shown in Formula II. The polyether $LiBF_4$ complex (2.9 % by weight) in a solution of diglyme was added to the BVE with stirring. The results are summarized in Table 2.

Example 25

An analogous procedure to that described in Example 1, except for the temperature of polymerization as noted in Table 3 below, was utilized for the polymerization of butyl vinyl ether (BVE) in the presence of a 0.15 wt% (based on the weight of vinyl ether) of the complex of $LiBF_4$ with triglyme (triethylene glycol dimethyl ether), as shown in Formula II. The polyether $LiBF_4$ complex (29 % by weight) in a solution of triglyme was added to the BVE with stirring. The results are summarized in Table 3. No significant polymerization occurred when the reactants were held at 25 °C for 36 hours prior to the heating at 70 °C for 300 minutes.

Table 1

Examples of Vinyl Ether Polymerization in the Presence of the Complex of $LiBF_4$ with Monoglyme

Ex. #.	Monomer	Wt% of Polyether $LiBF_4$ Complex[1]	Temp. (°C)	Time (minutes)	% Yield	Molecular Weight	Polymer State
1	BVE	0.29	50	40	93	101,000	thick resin
2	BVE	0.86	50	10	89	103,000	thick resin
3	BVE with 5% PTVE	0.14	70	120	100	not measurable	cross-linked solid
4	BVE	2.28	20	50	89	78,000	thick resin
5	EVE	0.29	70	10	86	95,000	thick resin
6	DDVE	0.03	70	120	100	not measurable	cross-linked solid
7	DDVE	0.29	20	300	100	not measurable	cross-linked solid
8	EDVE	0.29	70	50	100	not measurable	cross-linked solid
9	CHE	0.29	50	5	93	87,000	resin
10	PVE	0.29	40	5	94	98,000	resin
11	VPC	0.29	60	300	100	105,000	resin
12	VGE	0.29	50	120	100	not measurable	cross-linked solid
13	VGE	0.29	30	120	100	not measurable	cross-linked solid
14	DEDA	2.00	20	120	100	not measurable	cross-linked solid
15	VDA	2.00	20	120	100	87,000	solid
16	VADE	2.00	70	100	68	2,700	liquid resin
17	VPDE	0.57	20	30	88	2,300	liquid resin
18	FVE	2.00	70	300	58	1,600	liquid resin
19	TDVE	0.29	70	50	100	not measurable	cross-linked solid
20	BDDVE	0.29	60	40	100	not measurable	cross-linked solid
21	TVE	2.00	20	120	100	80,000	thick resin
22	BDVE	0.29	60	200	100	92,000	thick resin
23	PGVGE	0.29	60	100	100	not measurable	cross-linked solid

[1] Calculated based on the weight of the one or more vinyl ethers

Table 2

Example of Vinyl Ether Polymerization in the Presence of the Complex of $LiBF_4$ with Diglyme

Ex. #.	Monomer	Wt% of Polyether $LiBF_4$ Complex[1]	Temp. (°C)	Time (minutes)	% Yield	Molecular Weight	Polymer State
24	BVE	0.87	70	300	86	74,000	resin

[1] Calculated based on the weight of the one or more vinyl ethers

Table 3 Example of Vinyl Ether Polymerization in the Presence of the Complex of $LiBF_4$ with Triglyme							
Ex. #.	Monomer	Wt% of Polyether $LiBF_4$ Complex[1]	Temp. (°C)	Time (minutes)	% Yield	Molecular Weight	Polymer State
25	BVE	0.15	70	300	86	80,000	resin
[1] Calculated based on the weight of the one or more vinyl ethers							

Thus, the method of this invention is effective in the polymerization of vinyl ethers. By utilizing a complex of a lithium salt and a polyether as the catalyst, a temperature-activated latent catalyst, which is only slightly active at 25 °C, and preferably inactive at 25 °C, and which enables the control of the polymerization process over a wide temperature range with a rapid acceleration at a temperature above 35 °C, such as for example above 50 °C, is obtained. This allows the method to be carried out under mild conditions without overheating, excessive side reactions, and local polymerization, thus providing for high quality, high molecular weight polymers in high yield and also for utilization in applications where heat activation to form a poly(vinyl ether) is desired.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made without departing from the spirit and scope thereof.

CLAIMS

1. A method for the polymerization of one or more vinyl ethers to form a poly(vinyl ether), comprising the steps of:

   (i) providing said one or more vinyl ethers;

   (ii) providing a complex of a lithium salt and a polyether;

   (iii) forming a mixture of said one or more vinyl ethers and said complex, wherein said one or more vinyl ethers are present in a liquid phase, and wherein said complex is present in an amount of 0.01 to 2.5 per cent by weight of said one or more vinyl ethers; and,

   (iv) heating said mixture at a temperature sufficient to polymerize said one or more vinyl ethers and form said poly(vinyl ether).

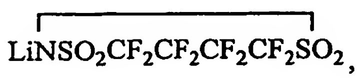
2. The method of claim 1, wherein said complex is present in an amount of 0.01 to 2.0 per cent by weight of said one or more vinyl ethers.

3. The method of claim 1, wherein said complex is present in an amount of 0.01 to 0.9 per cent by weight of said one or more vinyl ethers.

4. The method of claim 1, wherein said complex is present in an amount of 0.01 to 0.3 per cent by weight of said one or more vinyl ethers.

5. The method of claim 1, wherein said lithium salt is selected from the group consisting of:

$LiBF_4$, $LiSO_3CF_3$, $LiSO_3CF_2CF_3$, $LiSO_3CF_2CF_2CF_3$, $LiN(SO_2CF_3)_2$, $LiPF_6$, $LiAlCl_4$, $LiAsF_6$, $LiSbF_6$, $LiSbCl_6$, $LiClO_4$, $LiSO_3CH_3$, $LiC(SO_2CF_3)_3$,



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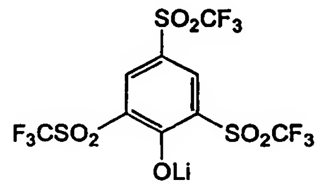

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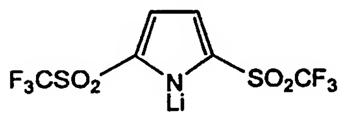

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6. The method of claim 1, wherein said lithium salt is lithium tetrafluoroborate.

7. The method of claim 1, wherein said lithium salt is a lithium perfluoroalkylsulfonate.

8. The method of claim 1, wherein said lithium salt is lithium triflate.

9. The method of claim 1, wherein said lithium salt is lithium imide.

10. The method of claim 1, wherein said polyether is an aliphatic polyether having two or more ether functional groups, wherein at least two of said two or more ether functional groups are characterized by an oxygen atom covalently bonded via single bonds to a first carbon atom and a second carbon atom, each of said first and second carbon atoms further covalently bonded via single bonds to three atoms selected from the group consisting of: carbon, hydrogen, oxygen, chlorine, fluorine and bromine.

11. The method of claim 10, wherein said polyether further comprises a vinyl ether group.

12. The method of claim 10, wherein said polyether further comprises two vinyl ether groups.

13. The method of claim 1, wherein said polyether is a glyme.

14. The method of claim 1, wherein said polyether is monoglyme.

15. The method of claim 1, wherein said polyether is diglyme.

16. The method of claim 1, wherein said polyether is triglyme.

17. The method of claim 1, wherein said polyether is tetraglyme.

18. The method of claim 1, wherein the molar ratio of said polyether to said lithium salt in said complex is 2 to 1.

19. The method of claim 1, wherein the molar ratio of said polyether to said lithium salt in said complex is 1 to 1.

20. The method of claim 1, wherein the molar ratio of said polyether to said lithium salt in said complex is less than 1 to 1.

21. The method of claim 1, wherein at least one of said one or more vinyl ethers is a monovinyl ether.

22. The method of claim 1, wherein at least one of said one or more vinyl ethers is a monovinyl ether selected from the group consisting of:

(a) methyl vinyl ether,
(b) ethyl vinyl ether,
(c) propyl vinyl ether,
(d) butyl vinyl ether,
(e) isobutyl vinyl ether,
(f) 2-ethylhexyl vinyl ether,

(g) cyclohexyl vinyl ether,

(h) 2,2,3,3-tetrafluoropropanol vinyl ether,

(i) ethylene glycol vinyl glycidyl ether,

(j) propylene glycol vinyl glycidyl ether,

(k) 3-(2-vinyloxyethoxy)propylene-1,2-carbonate,

(l) triethylene glycol vinyl ether ,

(m) 1,4-butanediol vinyl ether,

(n) vinyl ether of diethylene glycol diacetal,

(o) vinyl ether of diethylene glycol triacetal,

(p) vinyl allyl diether of ethylene glycol, and,

(q) vinyl propargyl diether of ethylene glycol.

23. The method of claim 1, wherein at least one of said one or more vinyl ethers is a divinyl ether.

24. The method of claim 1, wherein at least one of said one or more vinyl ethers is a divinyl ether selected from the group consisting of:

(a) ethylene glycol divinyl ether,

(b) 1,4-butanediol divinyl ether,

(c) diethylene glycol divinyl ether,

(d) triethylene glycol divinyl ether,

(e) tetraethylene glycol divinyl ether,

(f) 1,4-cyclohexanedimethanol divinyl ether,

(g) diethylene glycol diacetal divinyl ether, and,

(h) diethylene glycol triacetal divinyl ether.

25. The method of claim 1, wherein said mixture further comprises a solvent.

26. The method of claim 25, wherein said solvent comprises a polyether.

27. The method of claim 25, wherein said solvent comprises a polyether which is the same as the polyether of said complex.

28. The method of claim 27, wherein said complex is present in the amount of 1 to 35 per cent by weight of the polyether of said solvent.

29. The method of claim 1, wherein said temperature is from 20 °C to 120 °C.

30. The method of claim 10, wherein said temperature is from 20 °C to 120 °C.

31. The method of claim 28, wherein said temperature is from 20 °C to 120 °C.

32. The method of claim 1, wherein said temperature is from 35 °C to 120 °C.

33. The method of claim 1, wherein said temperature is from 50 °C to 120 °C.

34. The method of claim 1, wherein said temperature is from 70 °C to 120 °C.

35. A method for the polymerization of one or more vinyl ethers to form a poly(vinyl ether), comprising the steps of:

(i) providing said one or more vinyl ethers;

(ii) providing a complex of a lithium salt and a polyether;

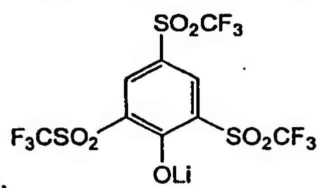
(iii) forming, at a first temperature of about 25 °C or lower, a mixture of said one or more vinyl ethers and said complex, wherein said one or more vinyl ethers are present in a liquid phase, and wherein said mixture does not significantly polymerize if kept at a temperature of 25 °C over a period of 36 hours; and,

(iv) subsequently heating said mixture to a second temperature greater than 35 °C to polymerize said one or more vinyl ethers and form said poly(vinyl ether).

36. The method of claim 35 wherein said lithium salt is selected from the group consisting of:

$LiBF_4$, $LiSO_3CF_3$, $LiSO_3CF_2CF_3$, $LiSO_3CF_2CF_2CF_3$, $LiN(SO_2CF_3)_2$, $LiPF_6$, $LiAlCl_4$, $LiAsF_6$, $LiSbF_6$, $LiSbCl_6$, $LiClO_4$, $LiSO_3CH_3$, $LiC(SO_2CF_3)_3$,

$\overline{LiNSO_2CF_2CF_2CF_2CF_2SO_2}$,



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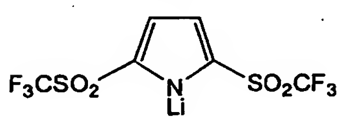

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37. The method of claim 35, wherein said lithium salt is lithium tetrafluoroborate.

38. The method of claim 35, wherein said lithium salt is a lithium perfluoroalkylsulfonate.

39. The method of claim 35, wherein said lithium salt is lithium triflate.

40. The method of claim 35, wherein said lithium salt is lithium imide.

41. The method of claim 35, wherein said polyether is an aliphatic polyether having two or more ether functional groups, wherein at least two of said two or more ether functional groups are characterized by an oxygen atom covalently bonded via single bonds to a first carbon atom and a second carbon atom, each of said first and second carbon atoms further covalently bonded via single bonds to three atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine, fluorine and bromine.

42. The method of claim 41, wherein said polyether further comprises a vinyl ether group.

43. The method of claim 41, wherein said polyether further comprises two vinyl ether groups.

44. The method of claim 35, wherein said polyether is a glyme.

45. The method of claim 35, wherein said mixture further comprises a solvent.

46. The method of claim 45, wherein said solvent comprises a polyether, which polyether in said solvent is the same as the polyether of said complex, and wherein said complex is present in the amount of 1 to 35 per cent by weight of said polyether in said solvent.

47. The method of claim 35, wherein said second temperature is from 35 °C to 120 °C.

48. The method of claim 35, wherein said second temperature is from 50 °C to 120 °C.

49. The method of claim 35, wherein said second temperature is from 70 °C to 120 °C.

50. The method of claim 35, wherein said second temperature is 50 °C or greater.

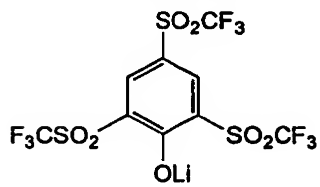
51. The method of claim 35, wherein said second temperature is 70 °C or greater.

52. A method for the polymerization of one or more vinyl ethers to form a poly(vinyl ether), comprising the steps of:

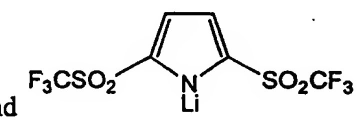
(i) providing said one or more vinyl ethers, wherein at least one of said one or more vinyl ethers is selected from the group consisting of:

(a) methyl vinyl ether,
(b) ethyl vinyl ether,
(c) propyl vinyl ether ,
(d) butyl vinyl ether,
(e) isobutyl vinyl ether,
(f) 2-ethylhexyl vinyl ether,
(g) cyclohexyl vinyl ether,
(h) 2,2,3,3-tetrafluoropropanol vinyl ether,
(i) ethylene glycol vinyl glycidyl ether,
(j) propylene glycol vinyl glycidyl ether,
(k) 3-(2-vinyloxyethoxy)propylene-1,2-carbonate,
(l) triethylene glycol vinyl ether,
(m) 1,4-butanediol vinyl ether,
(n) vinyl ether of diethylene glycol diacetal,
(o) vinyl ether of diethylene glycol triacetal,
(p) vinyl allyl diether of ethylene glycol,
(q) vinyl propargyl diether of ethylene glycol,
(r) ethylene glycol divinyl ether,
(s) 1,4-butanediol divinyl ether,
(t) diethylene glycol divinyl ether,
(u) triethylene glycol divinyl ether,
(v) tetraethylene glycol divinyl ether,
(w) 1,4-cyclohexanedimethanol divinyl ether,
(x) diethylene glycol diacetal divinyl ether,
(y) diethylene glycol triacetal divinyl ether, and
(z) pentaerythritol tetravinyl ether;

(ii) providing a complex of a lithium salt and a polyether, wherein said lithium salt is selected from the group consisting of $LiBF_4$, $LiSO_3CF_3$, $LiSO_3CF_2CF_3$, $LiSO_3CF_2CF_2CF_3$, $LiN(SO_2CF_3)_2$, $LiPF_6$, $LiAlCl_4$, $LiAsF_6$, $LiSbF_6$, $LiSbCl_6$, $LiClO_4$, $LiSO_3CH_3$, $LiC(SO_2CF_3)_3$, $LiNSO_2CF_2CF_2CF_2CF_2SO_2$,



, and



;

wherein said polyether is an aliphatic polyether having two or more ether functional groups, wherein at least two of said two or more ether functional groups are characterized by an oxygen atom covalently bonded via single bonds to a first carbon atom and a second carbon atom, each of said first and second carbon atoms further covalently bonded via single bonds to three atoms selected from the group consisting of: carbon, hydrogen, oxygen, chlorine, fluorine and bromine;

(iii) forming a mixture of said one or more vinyl ethers and said complex, wherein said one or more vinyl ethers are present in a liquid phase, and wherein said complex is present in an amount of 0.01 to 2.0 per cent by weight of said one or more vinyl ethers; and,

(iv) heating said mixture to at a temperature from 20 °C to 120 °C to polymerize said one or more vinyl ethers and form said poly(vinyl ether).

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/12086

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F16/12 C08F4/06 H01M10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 638 950 A (ENIRICERCHE SPA) 15 February 1995 (1995-02-15)	35-37, 39,41, 44,45, 47,48,50
	claims 1-9,12,16	
A	examples 4,6	1-34,49, 51,52
	page 4, line 2-7	
Y	page 5, line 18-20	38,40
	page 4, line 57 -page 5, line 3	

A	EP 0 774 795 A (ENIRICERCHE SPA ;OLIVETTI PERSONAL COMP SPA (IT)) 21 May 1997 (1997-05-21)	1-52
Y	claims 1,2	38,40
	examples 1,2	
	column 2, line 55 -column 3, line 13	
	column 4, line 22-25	

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 1999	18/10/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rose, E

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Inte 'onal Application No
PCT/US 99/12086

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 766 331 A (ENIRICERCHE SPA ;OLIVETTI PERSONAL COMP SPA (IT)) 2 April 1997 (1997-04-02)	1-52
Y	claims 1-4 examples 1,2 page 3, line 6-14	38,40

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte 'ional Application No

PCT/US 99/12086

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			JP	9180706	A	11-07-1997
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